

RECOMMENDATIONS

of the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques

15-18 September 2003, Toronto

The scientists present at the 12th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, September 15-18, 2003 in Toronto, recommend the following procedures and actions, in order to achieve the adopted WMO goals for global network comparability among different laboratories and various components as summarised in Table 1. The term “network precision” used in earlier recommendations has been replaced by the term “network comparability”. Definitions of terms concerning precision, accuracy etc. are given in Table 2.

Table 1: Recommended inter-laboratory (network) comparability of components discussed

Component	Inter-laboratory comparability
CO ₂	± 0.1 ppm (± 0.05 ppm in the southern hemisphere)
δ ¹³ C-CO ₂	± 0.01 ‰
δ ¹⁸ O-CO ₂	± 0.05 ‰
δ ¹⁴ C-CO ₂	± 2 ‰
O ₂ /N ₂	± 1 per meg
CH ₄	± 2 ppb
CO	± 2 ppb
N ₂ O	± 0.2 ppb

Table 2: Definitions of terms related to data quality

Term	Definition	Ref.
Accuracy (of a test method)	The closeness of agreement between a test result and the accepted reference value. ^(a)	[1]
Comparability	Mean difference between two sets of measurements, which should be within given limits. ^(b)	
Bias	The difference between the expectation of the test results and an accepted reference value.	[2]
Precision	Degree of internal agreement among independent measurements made under specific conditions. ^(c)	[2]
Repeatability (of results of measurements)	Closeness of the agreement between the results of successive measurements of the same measure and carried out under the same conditions of measurement. ^(d)	[2]
Reproducibility (of results of measurements)	Closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement. ^(d)	[2]
Uncertainty (Standard uncertainty)	A parameter associated with the result of a measurement that characterises the dispersion of values that could reasonably be attributed to the measure and. ^(e,f) (Uncertainty of the result of a measurement expressed as a standard deviation)	[2] [3]

^(a) Note that accuracy and precision are qualitative concepts and should be avoided in quantitative expressions.

^(b) 1. For example, difference in a comparison of measurements of a species in a discrete sample with the hourly average for the same hour in which the discrete sample was collected.

2. In the case of significantly different variances of the two sample sets, the difference of the mean may not be meaningful. The Wilcoxon-Mann-Whitney test can be used to test for statistical significance.

^(c) Precision must not be confused with accuracy or trueness. It is a measure for the dispersion of values.

^(d) Repeatability and reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results. In practice quantitative expressions of repeatability or reproducibility often refer to a dispersion of ± 1 standard deviations.

^(e) The concept of "uncertainty" is explained in detail in Ref. (3).

^(f) In practice the term "error (measurement error)" seems to be often used when actually "uncertainty" is meant. An error is viewed as having two components, a random and a systematic component (3). As further stated in Ref. (3), "error" is an idealised concept and errors cannot be known exactly. "Error" and "uncertainty" are not synonyms, but represent completely different concepts.

Recommendations are included in discussions under the following topic headings:

1. CO₂ calibration
2. CO₂ stable isotope calibrations
3. Radiocarbon in CO₂ calibration
4. O₂/N₂ calibration
5. CH₄ calibration
6. CO calibration
7. N₂O calibration
8. General recommendations for quality control of atmospheric measurements
9. General recommendations for data management and archiving
10. Summary of recent international planning of atmospheric trace gas measurement strategies

1. CO₂ CALIBRATION

1.1 Background

Round-robin comparisons of laboratory standards and comparisons of field measurements and samples over the last decade have regularly shown differences larger than the target comparability for merging data from different field sites (see Table 1). These systematic differences contribute to uncertainties in the location and magnitude of surface fluxes derived from atmospheric composition measurements. A CO₂ Central Calibration Laboratory (CCL) remains one of the fundamental components of the WMO strategy for addressing these problems.

1.2 The CO₂ Central Calibration Laboratory requirements

- a) The CCL maintains the WMO Mole Fraction Scale for Carbon Dioxide in Air by carrying out regular calibrations of this primary scale with an absolute method at approximately annual intervals. The primary scale shall range from approximately 180 ppm (covering atmospheric values in ice cores) to over 500 ppm (expected atmospheric background values in the latter part of the 21st century). The scale is currently embodied in a set of 15 CO₂-in-air mixtures in large high-pressure cylinders (called “WMO Primary Standards”).
- b) The CCL carries out comparisons with independent primary scales, established either through gravimetric, manometric, or other means. This includes an ongoing collaboration with the Scripps Institution of Oceanography (SIO) aimed at quantifying a potential shift of the WMO scale that may have occurred when the responsibility for maintenance of the scale was transferred from SIO to the Climate Monitoring and Diagnostics Laboratory (CMDL).
- c) The CCL provides complete and prompt disclosure of all data pertaining to the maintenance and transfer of the primary scale to the measurement laboratories participating in the WMO Global Atmosphere Watch (GAW) Programme.
- d) The CCL will update that scale when warranted, as the CO₂ mole fractions of the WMO Primary Standards become better known over time through repeated absolute measurements and comparisons. Revisions of the WMO Scale by the CCL must be distinguished by name, such as WMO X2003.
- e) The CCL provides calibrated reference gas mixtures of CO₂-in-air (called “transfer standards”) at the lowest possible cost.
- f) The CCL provides for a backup in case a catastrophic event occurs.
- g) In order to make possible a level of consistency among the CO₂ calibration scales of laboratories participating in the WMO GAW program of ± 0.03 ppm or less, the CCL shall aim to provide the calibrated standards for transfer of the primary scale to secondary and tertiary standards at that level of consistency.

1.3 Maintenance of calibration by GAW measurement laboratories

- a) All laboratories that participate in the GAW program must calibrate and report measurements relative to a single carefully maintained scale, the WMO Mole Fraction Scale for Carbon Dioxide in Air. Each GAW measurement laboratory must actively maintain its link to the WMO Scale by having its primary laboratory standards re-calibrated by the CCL every three years. It is recommended that the laboratory primary gases are kept for many years so that a calibration history can be built for each of them.
- b) Each GAW measurement laboratory should maintain a strictly hierarchical scheme of transferring the calibration of its laboratory primary gases to working standards, and from working standards to atmospheric measurements. Traceability via a unique path will, in principle, enable the unambiguous and efficient propagation of changes (including retro-active changes) in the assigned values of higher level reference gases all the way to measured values for atmospheric air.

- c) In order to minimise the risk of creating offsets that are coherent among laboratories within the same region, each laboratory should maintain the shortest possible direct link to the WMO Primary Standards.
- d) Because of ongoing improvements in measurement technology it is possible that individual laboratories or groups of laboratories may be able to maintain excellent precision and comparability in scale propagation from their laboratory primary standards to lower level standards, which could be beyond the precision with which laboratory primary standards can be tied to the WMO scale. Internal scales of this sort must also remain tied to the WMO scale to the extent possible.

1.4 Improving links to WMO Primary Standards

- a) CMDL organises round-robin comparisons of laboratory calibrations by distributing sets of high-pressure cylinders to be measured by participating laboratories. The round-robin comparisons are to be used for an assessment of how well the laboratories are maintaining their link to the WMO Mole Fraction Scale. They are not to be used for redefining laboratory calibration scales. We recommend that round-robins are repeated once every two years. However, comparisons of reference gases by themselves are not sufficient to ensure that atmospheric measurements are comparable to the degree that is required (see Section 8 on Quality Control).
- b) While scales can only be defined and maintained by an operational designated CCL, WMO and IAEA welcome efforts that monitor, confirm, or improve CCL links to primary reference materials or fundamental constants.
- c) In such cases, the WMO and IAEA Expert committees undertake the responsibility for the evaluation of the effectiveness of such measures and for recommending modifications to existing protocols.

2. CO₂ STABLE ISOTOPE CALIBRATION

Since the 11th CO₂ experts meeting 2001 in Tokyo, considerable progress has been made towards a tighter connection of the CO₂-in-air standards/references to the VPDB scale, which is one of the important activities initiated or endorsed by the Tokyo meeting. However, a consensus has not been achieved, regarding how to establish and maintain the traceability for isotope measurements of atmospheric CO₂ within the network comparability target (see Table 1) **via only one primary standard** (i.e. NBS19) on VPDB scale. There are a number of points in regard to this issue.

- a) The VPDB-CO₂ scale should remain the primary scale for expressing stable isotope ratio measurements of atmospheric CO₂, which is the link to the measurements involving major carbon reservoirs on the Earth surface (atmosphere, ocean, and terrestrial ecosystems).
- b) Results of CO₂-in-air samples with the CO₂ originating from NBS19, NBS18 and other widely recognized carbonate materials as new references have been presented by MPI-BGC Jena (work performed within the European TACOS Project). Measurement precision of ± 0.015 permil ($\delta^{13}\text{C}$) and ± 0.03 per mill ($\delta^{18}\text{O}$) respectively has been achieved. With a carbonate material close to NBS19 in most properties ('Mar-J1') the link to VPDB is considered appropriate. In order to prove that the CO₂ has not been changed by the mixing process, the NBS19-CO₂ in air should be measured against the pure CO₂ from NBS19, and the difference in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ should be close to or within the assigned network comparability (i.e. ± 0.01 permil for carbon and ± 0.05 permil for oxygen).
- c) CO₂ from carbonate materials other than NBS19 (e.g. IAEA-CO1, CO8 and CO9) as well as laboratory standards in greater supply such as CAL1 and CAL2 (MSC) should also be mixed into CO₂-free air in order to span a large range of isotopic compositions and provide a means for monitoring the stability and behaviour of laboratory working standards/references.

- d) NIES has prepared two large sets of CO₂ samples flame sealed in glass tubes with isotopic values close to air-CO₂ and to NBS19. Provided these samples can be measured with the required high precision of ± 0.015 and ± 0.03 permil in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively, they can serve as a medium term anchor of the difference between NBS19 and air-CO₂. For fulfilling such role, it should be proved that the values are well calibrated on the VPDB-CO₂ scale.
- e) It has been demonstrated that a reproducibility of about ± 0.015 permil in $\delta^{13}\text{C}$ and about ± 0.05 permil in $\delta^{18}\text{O}$ of carbonates can be consistently achieved over a period of several years. These values are close to the assigned network comparability requirement. Direct calibrations of air CO₂ lab standards on VPDB scale via the primary standard NBS19 and other IAEA recommended international standards (e.g. NBS18) should be encouraged since it is the shortest and most independent way to link lab-standards to the primary standard.
- f) The CSIRO/IAEA CLASSIC cylinders continue to be a valuable resource in particular to link past measurements to future CO₂-in-air reference materials which are expected to be better linked to VPDB and VSMOW scales.
- g) A version number with detailed documentation (i.e. including constants and equations used) should always accompany the assignment of in-house working standards/references to the VPDB scale, or changes to the assignment. The documentation should be available in the literature or public domain.
- h) New data on the N₂O correction suggest that more frequent checks should be made on the ionisation efficiency ratio of N₂O and CO₂. The finding requires further experiments. The adoption of a CO₂-in-air reference will render this correction less critical.
- i) Groups measuring absolute isotopic ratios in pure gases (e.g., the Institute for Reference Materials and Methods, Geel, Belgium) should be encouraged to work alongside the TACOS and similar programs to improve links between CO₂-in-air and carbonate standards, with the eventual aim of supplementing primary links of the CO₂-in-air measurements.
- j) A carbonate material in sufficient supply with isotopic values close to air-CO₂ is required as a long-term anchor of air-CO₂ measurements. The search for such material, as recommended by the 11th WMO/IAEA CO₂ experts meeting, is considered urgent. IAEA will enhance its efforts to locate and characterize such material.
- k) Due to the influence of plant and surface water on atmospheric CO₂ it is suggested to directly link ^{18}O of CO₂-in-air references to VSMOW instead of VPDB. This would eliminate the ambiguity of the VPDB scale resulting from the less precisely known fractionation factor of ^{18}O in CO₂-H₂O equilibrium. Activities to equilibrate CO₂-in-air with well-characterized water under tightly controlled conditions are endorsed and welcome to be presented at the 13th CO₂ experts meeting.

3. RADIOCARBON IN CO₂ CALIBRATION

Radiocarbon (^{14}C) observations in atmospheric CO₂ are gaining increased interest in carbon cycle research, in particular for budgeting regional fossil fuel CO₂ contributions/emissions. Standardisation of Radiocarbon analysis is well established in the Radiocarbon Dating Community since many years, and the New Oxalic Acid Standard (NIST SRM 4990C) has been agreed upon as the main Standard Reference Material. Other reference material of various origin and ^{14}C activity is available and distributed by e.g. IAEA.

In the atmosphere, recent $\Delta^{14}\text{C}$ gradients (north versus south in the free troposphere and marine vs. continental within hemispheres) are very small and on the order of general measurement precision, i.e. only several permil up to very few percent. The “detection limit” to derive regional fossil fuel contributions even with the highest measurement precision is thus only about 1 ppm at best. An intercomparison activity dedicated to ^{14}C laboratories participating in atmospheric $^{14}\text{CO}_2$ monitoring is, therefore, strongly recommended.

4. O₂/N₂ CALIBRATION

Twelve laboratories world-wide have been identified which make high-quality atmospheric O₂/N₂ measurements (see Annex 2). Currently there exists no common calibration scale, and small-scale intercomparison efforts have been undertaken by only a few laboratories. Participants were unanimous that significant efforts should now be taken to improve community-wide intercomparison.

In considering an ideal calibration and intercomparison programme, the following points were considered:

- a) Ultimately there is a need for a globally standardised calibration scale which all labs/field sites are linked to.
- b) One or more mechanisms are needed which provide quality assurance that data derived from flask measurements from one lab are comparable to data derived from flask measurements from a second lab.
- c) One or more mechanisms are needed which provide quality assurance that data derived from continuous measurements from one lab/field site are comparable to data derived from continuous measurements from a second lab/field site.
- d) Any calibration or intercomparison programme must take into account the fact that many different analyser techniques are currently used within the community to achieve high-precision O₂/N₂ measurements (e.g. interferometric, mass spectrometric, paramagnetic, VUV absorption, gas chromatographic, and electrochemical fuel cell).

Ten of the twelve O₂/N₂ labs (of Annex 2) were represented at this meeting, and the following recommendations were agreed upon by all participants:

- a) A “Round-Robin Cylinder” intercomparison programme will be initiated. This will consist of two sets of three high pressure cylinders to be analysed by all participating labs, with the two sets to rotate in opposite direction. At this stage we do not recommend that this programme should result in a common calibration scale, instead it should be used to establish and maintain a link between existing calibration scales. This decision should be reassessed at the 13th WMO/IAEA Experts Meeting in 2005.
- b) For those laboratories which make flask measurements, we will initiate a “Sausage Flasks Matrix” intercomparison programme. This will involve a primary laboratory simultaneously filling a pair of flasks from each participating laboratory from a high pressure cylinder and distributing to all labs for analysis.
- c) Although we did not formalise a programme, we strongly encourage all flask measurement laboratories to initiate or continue “Shared Flasks” intercomparison programmes. That is, programmes whereby two (or more) laboratories analyse sample air from a station site, either from exactly the same flasks, or from flasks filled simultaneously at a given site. The wider community at this meeting discussed the possibility of a “Super-Site”, where a single field station is used to link all flask analysis laboratories in such intercomparison programmes. If such a Super-Site is adopted, it would be wise for the O₂/N₂ community to adopt the same site.
- d) Ralph Keeling (SIO) agreed to be the “Primary Lab”, supplying all high pressure gas cylinders for the round-robin cylinder programme, and filling all flasks for the sausage flasks matrix programme.
- e) Andrew Manning (MPI-BGC) agreed to collate all data resulting from the two programmes.

5. CH₄ CALIBRATION

5.1 Background

There is currently no internationally-accepted standard scale for measurements of atmospheric methane. To make optimal use of existing measurements in studies of the global CH₄

budget, either all measurements must be on the same standard scale, or conversion factors must be determined to convert from one scale to another. Fortunately, many members of the CH₄ measurement community have compared their standard scales, and multiplicative factors have been determined that allow us to put many measurements on a common scale. This approach has been effectively used in the Co-operative Atmospheric Data Integration Project to produce GLOBALVIEW-CH₄. Despite this, the community would benefit from an internationally-accepted scale that is transferred to laboratories participating in the GAW network by a Central Calibration Laboratory.

5.2 Proposal for a CH₄ Central Calibration Laboratory (CCL)

NOAA CMDL has developed a gravimetrically-based CH₄ standard scale that covers the nominal range of 300-2600 nmole/mole CH₄, so it is suitable for measurements of CH₄ in glacial and interglacial ice cores, and at GAW background sites. At the 12th WMO/IAEA CO₂ Experts Meeting, there was general agreement that this new CMDL scale should define the WMO CH₄ mole fraction scale, and that CMDL should take on the role of CCL for CH₄; CMDL is also CCL for CO₂, CO, and N₂O. The estimated time frame for CMDL to assume the role of CH₄ CCL is mid-2004, after the details of the new gravimetric scale have been published. As with the other species, CMDL will transfer the CH₄ scale to GAW participants as well as to the WCCs at the lowest possible cost and with the smallest possible uncertainty. WCCs and QA/SACs undertake tasks and procedures for carrying out station system and performance audits and intercomparison in co-operation with the GAW Central Calibration Laboratory in the GAW network. EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA). Travelling standards used for methane audits at global GAW sites refer to the new CMDL scale. CMDL will continue CH₄ intercomparison as part of the CO₂ round-robin experiments.

6. CO CALIBRATION

6.1 Background

Being the major chemically active trace gas resulting from large scale natural and non-natural phenomena like biomass burning and fossil fuel combustion, and being a precursor gas for global background tropospheric ozone, CO is frequently measured. Most measurements are based on in situ analyses and the analysis of collected air samples. NOAA/CMDL provide a large and systematic set of observations at the surface, which forms by far the most important source of experimental information. Observations made during aircraft campaigns form the second most important database. At some sites, spectroscopic data allow, or have allowed, retrieval of information about the vertical distribution. Presently also satellite data are becoming available (MOPITT-TERRA, SCIAMACHY-ENVISAT, TESS-AURA), and the wide geographical coverage combined with a (be it limited) vertical resolution, at times combined with data assimilation models, enables for the first time 3D information about major pollution plumes to be constructed. In-situ, ground based measurements are important as they provide the high temporal resolution that cannot be achieved through either satellite or flask measurements.

6.2 Analytical

The present recommendations solely pertain to the calibration of non-remote sensing methods. The validation of remote sensing data is a complicated separate issue not treated here. Experience has shown, however, that even the accurate calibration of CO measurements based on chemical/physical methods is far from trivial. Basically, mixing ratios of 40 to 250 nmole/mole have to be determined with a standard uncertainty of ± 1 ppb.

Unlike CO₂, for CO there is a low degree of standardisation in analytical techniques deployed. There are in fact at least six analytical techniques in use. In (estimated) order of frequency of usage: (1-RGD) gas chromatography using a reduction gas detector, (2-GFC) gas filter correlation, (3-VUV) vacuum ultraviolet fluorescence, (4-FID) gas chromatography using methanization and a flame ionisation detector (FID), (5-TDLAS) Tunable Diode Laser Absorption

Spectroscopy, and sporadically (6-AVD) absolute volumetric determination. For the last 2 methods no instruments are commercially available.

The specific calibration problems for CO are that a) gravimetric mixtures have to be diluted to environmental levels, which introduces errors, and b) that at these levels CO mixing ratios in storage containers are not stable over time periods of years or longer. NOAA/CMDL's Carbon Cycle Group has on two occasions organised round-robin tests involving 5 to 10 laboratories. This has helped "the international CO community" enormously, but also exposed some drift and inconsistency in the NOAA/CMDL calibration scale.

It is noted that like for CO₂, CO mixing ratios in gas storage cylinders may change with time. The preparation of a gravimetric standard, does not *a priori* guarantee that the actual CO mixing ratio corresponds to the assumed one. There are two ways around this problem, namely either more extensive research in understanding the problems of stability of CO in storage cylinders, or volumetric measurements. Presently, only the Max-Planck-Institute for Chemistry, Mainz, Germany, carries out volumetric measurements of CO.

WMO has endeavoured to improve the international situation by starting to implement an audit system for CO measurements at GAW stations. Combining all experience gained so far, it is realistic to expect CO data to be expressed on one single scale that is traceable based on the mixing and dilution of CO in air, and that is occasionally verified independently by the absolute volumetric determination procedure used by the Max-Planck-Institute for Chemistry in Mainz, Germany. A realistic target for the standard uncertainty of measurements is at the 1% level. For establishing global trends, and to get a sufficiently accurate estimate of the tropospheric burden, it seems that 1% is both analytically attainable, and scientifically sufficient.

6.3 Recommendations

NOAA/CMDL is the CCL for carbon monoxide. In this capacity, they provide calibrated reference gas mixtures ('transfer standards') to laboratories participating in the GAW CO programme at the lowest possible cost. CO calibrations should be traced back to the scale maintained by NOAA/CMDL. This scale was revised in 2000, and all measurements at GAW stations should refer to the new scale. EMPA is the designated World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and is in charge of conducting system and performance audits including inter-comparisons at global GAW stations. Travelling standards used for audits at global GAW sites refer to the new CMDL scale. Round robins (organised by CMDL) showed some inconsistencies and/or drift in the CO scale. The Scientific Advisory Group (SAG) Reactive Gases is now being established, and is scheduled to meet in fall 2004. Further steps and recommendations will be co-ordinated by the SAG members.

7. N₂O CALIBRATION

7.1 Summary of the NOAA N₂O calibration scale

The NOAA 2000 N₂O scale was developed in 2000 from 17 gravimetric standards. Prior to 2000 the scale was based on six gravimetric standards prepared in 1993. Two of these were dropped from the 2000 set, as the cylinders were low in pressure. The set of 17 ppb-level standards contains four in the year 1993 gravimetrically prepared standards (in 29-L Aculife-treated aluminium cylinders) and 13 in the year 2000 gravimetrically prepared standards (in 5.9-L untreated aluminium cylinders obtained from Scott-Marrin Inc.). The set was derived from three different ppm-level standards, all of which were prepared from 99.9% N₂O (Scott Specialty Gases). The 1993 standards were prepared with Air Products zero air, scrubbed with 1-L traps of molecular sieve and Amborsorb. The 2000 standards were prepared using Linweld ultra high purity zero air scrubbed with molecular sieve and Amborsorb, plus two additional 150 cc traps of molecular sieve and activated charcoal chilled to 0°C. All gravimetrically prepared standards in 2000 contain CO₂ (330-380 ppm) and SF₆ (1-6 ppt). The 1993 standards contain CO₂ (350–400 ppm) and highly variable SF₆ (0-40 ppt).

In 2002, an Agilent 6890 gas chromatograph was configured for N₂O/SF₆ analysis.

Column: 3/16", Porapak Q, 3m main, 2m backflush
ECD: Agilent, 340 deg C
Oven: 56 deg C
Carrier: N₂ (45 cc/min main, 45 cc/min backflush), doped with 0.05 cc/min CO₂
Sample loop: 9 cc
GSV: Valco 12-port
Typical repeatability 0.1-0.2 ppb (1 s.d.)

The precision of the Agilent/N₂ system has proved to be better than that of the previously used Valco/P5 system (operated with 95% Ar/ 5% CH₄ as carrier gas). More importantly, this instrument has proved to be more stable over changes in operating conditions and carrier gas.

At NOAA, primary standards are prepared gravimetrically as described above. Secondary standards are dilutions of free tropospheric air obtained from Niwot Ridge, Colorado, USA, for which concentrations are determined by reference to the primary standard curve. Secondary Standards are used to calibrate Tertiary Standards for distribution to NOAA sites and laboratories. It is the NOAA Tertiary Standards that are used as Laboratory Standards by the World Calibration Centre (WCC) and any participating laboratories.

A set of laboratory standards with five different N₂O mole fractions calibrated by NOAA should be obtained by each GAW station and should serve as the station's highest-level standards. These are to be safeguarded, used only for infrequent calibrations of working standards or reference gas, and they should be recalibrated by NOAA every 5 years. Working standards at each laboratory can be either appropriately prepared synthetic gas mixtures or dried ambient air compressed into high-pressure aluminium cylinders. Besides N₂O, synthetic mixtures should contain atmospheric levels of N₂, O₂, and CO₂ as a minimum. For the use at a GAW station these have to be calibrated by comparison with the station's set of primary laboratory standards or an equivalent set of standards traceable to the NOAA CMDL scale.

The mean interhemispheric difference in N₂O mole fraction is around 1 ppb and the pole-to-pole difference is 2 ppb. These global differences are 0.3-0.6% of the recent mean mole fraction of N₂O in the atmosphere, which requires not only high precision of measurements, but also high consistency among assigned values for standards. Ideally, the expanded uncertainty would be ± 0.1 ppb or better, but this may prove too difficult a goal to meet in the short term.

Currently, NOAA maintains its scale by analysing 17 primary standards annually, and five secondary standards over the 280-350 ppb range weekly. A second working standard (310 ppb) is run weekly as a secondary check on uncertainties. Precision (1 standard deviation) normally varies between ± 0.02 and $\pm 0.1\%$. An analytical precision of $\pm 0.02\%$ produces an uncertainty in predicting an unknown from a 5-standard curve of ca. ± 0.1 ppb near ambient values and ± 0.13 resp. ± 0.15 ppb at 250 and 350 ppb. However, at present, the precision does not hold at 0.02% over the long term. At this time, consistency for assigning values to standards can be guaranteed at ± 0.3 ppb, although ± 0.2 ppb is a realistic short-term goal. Consistency of ± 0.1 ppb among standards should be attainable in the long term.

7.2 Participating Laboratories and Field Sites

For most N₂O systems, the repeatability (2 standard deviations) of the gas chromatographic method under ambient sampling is expected to be better than $\pm 1\%$ (± 3 ppb). A value of at least $\pm 0.2\%$ (± 0.6 ppb) should be aimed at for all GAW stations. With high-quality equipment and maintenance, a precision of $\pm 0.08\%$ (± 0.3 ppb) can be achieved. Precision should be determined from multiple, interspersed analyses of a gas of constant N₂O mole fraction (e.g. working standard) during routine operation.

For basic calibration of the analytical system and for intercomparison, five different N₂O mole fractions ranging between 290 and 350 ppb should be used. This will determine the response curve of the ECD. Working standards should be compared with laboratory standards at least twice a year. It is recommended to run analyses of samples of assigned N₂O mole fraction from a "target cylinder" once per day or more frequently. This will enable early detection of minor malfunctions of the analytical system. These and other analytical and quality control procedures are discussed in detail in the Measurement Guidelines / Data Quality Objectives for N₂O, which are currently being edited by the SAG GG (Report in preparation).

8. GENERAL RECOMMENDATIONS FOR QUALITY CONTROL OF ATMOSPHERIC MEASUREMENTS

- a) Besides round-robin comparisons, more frequent intercomparison activities between pairs of laboratories, which for example also more closely simulate the analyses of actual air samples, such as flask air intercomparison (ICP) experiments are strongly recommended. The tremendous benefit of routine intercomparison has been demonstrated (ref. 4) and is reinforced. Mutual exchange of air in glass flasks is encouraged as a means to detect experimental deficiencies at an early stage and remove discrepancies in the results fast.
- b) Intercomparison programs distributing to a larger number of laboratories flasks filled in series from tank air as a "sausage" as initiated by the European TACOS project (ref. 5) are able to increase the benefit of mutual flask exchange.
- c) Another possibility to link several laboratories in one single intercomparison exercise is the establishment of "Super Sites", field stations which could take on the task to fill a larger number of flasks regularly and simultaneously with ambient air and distribute them to participating laboratories.
- d) Clear protocols and reports of experience gained in intercomparison projects should be provided. Results should be published in the peer-reviewed literature. The evaluation of such activities and recommendations for refinement, co-ordination and expansion of such activities has been accepted as a key responsibility of future WMO/IAEA Expert meetings.
- e) The participants of the WMO/IAEA Experts meeting strongly support the IHALICE intercomparison initiative which also includes CO₂, CH₄, CO, N₂O and SF₆.

9. GENERAL RECOMMENDATIONS FOR DATA MANAGEMENT AND ARCHIVING

9.1 Data Management

All GAW measurement laboratories regardless of program size are required to manage all new and existing atmospheric trace gas and supporting (meta) data using a database management strategy (DBMS) that meets or exceeds the following criteria

- a) demonstrates that mixing/isotope ratios can be unambiguously and automatically reproduced from raw data at any time in the future
- b) demonstrates that revisions to a laboratory's internal calibration scale can be efficiently and unambiguously propagated throughout the database
- c) supports routine and automatic database updates of all measurement and meta data
- d) ensures that all data reside locally, in a single location, and are centrally accessible to internal users
- e) ensures fast and efficient retrieval of all data
- f) maximises users' ability to assess data quality
- g) facilitates data exploration
- h) minimises the risk of data loss or corruption due to theft, misuse, or hardware/software failure
- i) maximises security to primary data (e.g., data from which all processed data is derived)
- j) supports routine and automatic backup of all data
- k) supports complete data recovery in the event of catastrophic data loss

GAW measurement laboratories are encouraged to use WMO document #150 as a guideline in developing and implementing an atmospheric data management strategy.

9.2 Data Archiving

Laboratories participating in the WMO-GAW program must submit their data regularly to the World Data Centre for Greenhouse Gases (WDCGG). A co-ordinated annual submission of data, with clearly identified version number and supporting details is strongly recommended. The same recommendation holds to other public-access data archive centres such as the Carbon Dioxide Information Analysis Centre (CDIAC).

9.3 Co-operative Data Products

All laboratories making high-quality atmospheric carbon dioxide and methane measurements are strongly encouraged to participate in the Co-operative Atmospheric Data Integration Project which produces the GLOBALVIEW data products. The majority of current participants provide updates in May that include data through December of the preceding year. Data contributed to the GLOBALVIEW project are used to derive the data product. The product includes no actual data.

10. SUMMARY OF RECENT INTERNATIONAL PLANNING OF ATMOSPHERIC TRACE GAS MEASUREMENT STRATEGIES.

This report is prepared in the context of widespread governmental acceptance of climate change (United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto protocol), and leads to new and urgent challenges to the carbon cycle community. Two main objectives justify the deployment of atmospheric observations:

1. To quantify the present state of the fluxes of greenhouse gases and better understand the controlling processes.

2. To monitor and assess the effectiveness of emission control and/or reduction activities on atmospheric levels, including attribution of sources and sinks by region and sector.

International scientific planning has been co-ordinated by the Global Carbon Project (GCP) (<http://www.globalcarbonproject.org/>) combining the efforts of International Geosphere-Biosphere Project (IGBP), World Climate Research Project (WCRP) and International Human Dimensions Programme (IHDP). The GCP produced in 2003 a Science Implementation Plan dealing with the patterns and variability of carbon fluxes, the associated processes and feedback, and the management of the carbon cycle. GCP identified both systematic observations of concentrations in the atmosphere and oceans and process oriented carbon cycle observations. In parallel, the Integrated Global Carbon Observing Strategy Partnership (IGOS-P) has formed a Theme Team called IGCO (Integrated Global Carbon Observation) to report on those systematic global carbon observational networks that can form the backbone of a future monitoring system, building upon earlier planning by GTOS/TCO (Terrestrial carbon Observations <http://www.fao.org/gtos/TCO.html>) and GOOS (Global Ocean Observing System <http://ioc.unesco.org/goos/>). The IGCO Theme Team task is to establish data requirements, design network configurations, and develop advanced algorithms for carbon observations, which will be the core of a future, sustained observing system by 2015.

In both GCP and IGCO documents, a strong atmospheric observing component is outlined as indispensable to link land and ocean observing components and to integrate across spatial heterogeneities and temporal variability of local flux information. A modelling strategy for developing Carbon Cycle Data Assimilation schemes that will interpret observations in terms of fluxes is also outlined, based upon a combination of data and models for the different domains: atmosphere, ocean and land, where results from one domain place valuable constraints on the workings of the other two ("multiple constraint").

There are two major novel developments in the planning of atmospheric trace gas measurement strategies since the former WMO meeting in Tokyo in 2001

The Orbital Carbon Observatory (OCO) satellite mission from NASA is scheduled for launch in 2007 and expected to deliver the first global coverage of column integrated CO₂ measurements using differential absorption in the short wave infrared region of the spectrum. The target precision of OCO measurements is ± 1 ppm but there are a number of potential sources of bias in the remotely sensed CO₂ data that call for specific in situ validation measurements, in particular high-quality vertical profiles.

New major regional programmes have received funding to increase the density of atmospheric trace gas observations and terrestrial carbon observations over North America (NACP; <http://www.esig.ucar.edu/nacp/>) and Western Europe (CARBOEUROPE ; <http://www.bgc-jena.mpg.de/public/carboeur/>). It is important that those regional programmes remain tightly linked to the international GAW effort and produce regional data sets that can be merged safely into an enhanced global picture of carbon sources and sinks.

Lessons from such regional initiatives should be valuable to formulate future atmospheric observing strategies for the remaining under-sampled regions, in particular in the Tropics. The strong commitment to development of expertise in developing countries by WMO and IAEA, including the establishment of high-quality measurement capabilities, remains a critical issue for achieving adequate spatial coverage of the globe in the coming decade.

Plans for future carbon observing networks are to a large extent based on anticipated advances in modelling, inversion, and data assimilation techniques to make use of higher resolution and higher variability data. Because these analytical tools are still in development it is difficult to quantitatively assess the success of various planned observing system enhancements. Nevertheless, existing and prototype modelling systems can be used for guidance on where we should be concentrating our precious resources. Critical questions to address include the relative benefit of a few very high accuracy measurements versus many somewhat lower accuracy measurements, the trade-off between low cost flask measurements and more expensive continuous measurements, the value of high-variability and high-signal continental boundary-layer data relative to lower-variability but lower-signal marine boundary layer and free troposphere data, the importance of vertical profile data for constraining CO₂ fluxes and testing boundary-layer parameterizations in comparison to striving for denser surface coverage, and the benefits of including measurements of other species. Thus we should continue to support efforts at quantitative network optimisation, such as the NCAR C-DAS (National Centre of Atmospheric Research Carbon Data-Model Assimilation, <http://www.cdass.ucar.edu/>) and observing system simulation experiments (OSSE).

Ideally we would have these questions answered before we committed significant resources to a particular strategy, but we only get one chance to sample the atmosphere so it is well justified to expand the observations before the analytical tools are mature. While we must presently rely on less sophisticated network design exercises, calculations, and reasoning, we have reasonable confidence in a number of basic parameters describing the optimal future carbon observing system.

The following observational strategies seem to be most promising in this context:

- a) Expand aircraft flights over vegetated areas not sampled or under sampled, with priority to tropical South America, Africa, South East Asia. Higher altitude flights shall be needed to cope with vigorous convective mixing up to 10 km in the tropics. For that purpose, the use of passenger aircraft such as pioneered in atmospheric chemistry (CARIBIC, MOZAIC programmes) should be promoted.
- b) Carry out continuous measurements in the boundary layer, in particular on top of high towers, and further pursue the option to use eddy flux towers as a platform for additional

- precise CO₂ mixing ratio observations (ref. 6). These observations will enable us to quantify regional sources and sinks by means of inverse modelling.
- c) Carry out in the vicinity of continuous tower based boundary layer measurement sites frequent vertical profiles if possible under all weather conditions, that will quantify the vertical mixing of surface sources and sink fluxes.
 - d) Develop high-quality measurements of carbon cycle tracers that can be used to attribute natural fluxes to their controlling processes (¹³CO₂, O₂/N₂, ¹⁸OCO) and separate fossil fuel emissions (¹⁴CO₂, CO...)
 - e) Develop high-quality measurements of transport tracers (SF₆, ²²²Rn, C₂Cl₄...) in order to validate numerical models of atmospheric transport, in particular their vertical mixing.
 - f) Report actual uncertainties on individual data where available. In particular, pursue the development of data products for modellers (e.g. GLOBALVIEW) that can include wherever possible information on representativeness, calibration offsets, etc...
 - g) Plan atmospheric measurements jointly with terrestrial and oceanic process communities to optimise the link of atmospheric composition change to surface processes. For example, the development of the "virtual tall tower" concept to use short towers as part of atmospheric networks, and the synergetic use of ocean pCO₂ surveys programmes to make atmospheric measurements.
 - h) Encourage and facilitate the development of improved atmospheric tracer transport models. Among the identifiable needs are improving the representation of atmospheric convection, the representation of the surface boundary layer and the need to improve spatial resolution to better account for sources and sinks heterogeneity. Equally as important for assessing the distribution of fluxes is the use of several independently developed models and their frequent intercomparison. Finally, it is important to develop and maintain community models which are numerically efficient, which can run from standard computer platforms with a modest amount of training, and which are made available to the scientific community as a whole.

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ABBREVIATIONS AND ACRONYMS USED IN THIS REPORT

AVD	Absolute Volumetric Determination
CARBOEUROPE	Programme regrouping ecosystem and atmospheric research on the carbon balance of Europe (EU funded project)
CARIBIC	Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container
CCL	Central Calibration Laboratory
CDIAC	Carbon Dioxide Information Analysis Centre
CLASSIC	Circulation of Laboratory Air Standards for Stable Isotope inter Comparisons
CMDL	Climate Monitoring and Diagnostics Laboratory, Boulder, CO, U.S.A.
CSIRO	Commonwealth Scientific & Industrial Research Organisation
DBMS	Data Base Management Strategy
ECD	Electron Capture Detector
EMPA	Eidgenössische MaterialprüfungsAnstalt
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch (WMO Program)
GCP	Global Carbon Project
GG	Greenhouse Gases
GLOBALVIEW	Co-operative Atmospheric Data Integration Project
GOOS	Global Ocean Observing System
GTOS	Global Terrestrial Observing System
IAEA	International Atomic Energy Agency
ICP	InterComparison Project
IGBP	International Geosphere-Biosphere Programme
IGCO	Integrated Global Carbon Observation
IHALICE	International HALocarbon in Air Comparison Experiment
IHDP	International Human Dimensions Programme
MOPITT-TERRA	Measurements Of Pollution In The Troposphere
MOZAIC	Measurement of ozone, water vapour, carbon monoxide and nitrogen oxides aboard Airbus in-service aircraft
MPI-BGC	Max-Planck Institut für Biogeochemie, Jena, Germany
MSC	Meteorological Service of Canada
NACP	The North American Carbon Program
NCAR C-DAS	National Centre for Atmospheric Research Carbon Data-Model Assimilation
NIES	National Institute for Environmental Studies, Tsukuba, Japan
NIST	National Institute of Standards and Technology
OCO	Orbital Carbon Observatory
OSSE	Observing System Simulation Experiment
QA/SAC	Quality Assurance/Science Activity Centre
RGD	Reduction Gas Detector
SAG	Scientific Advisory Group
SCIAMACHY	SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY
SIO	Scripps Institution of Oceanography
SRM	Standard Reference Material
TACOS	Terrestrial and Atmospheric Carbon Observing System -Infrastructure (EU funded project)
TCO	Terrestrial Carbon Observations
TDLAS	Tunable Diode Laser Absorption Spectroscopy
UNFCCC	United Nations Framework Convention on Climate Change
VPDB	Vienna Pee Dee Belemnite (Isotope Standard)

VSMOW	Vienna Standard Mean Ocean Water (Isotope Standard)
VUV	Vacuum UltraViolet (Fluorescence)
WCC	World Calibration Centre
WCRP	World Climate Research Programme
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization

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